Ammoxidation of Straw Pulp Alkaline Lignin by Hydrogen Peroxide with Iron(II) Cation

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Ammoxidation of straw-pulp alkaline lignin using hydrogen peroxide as oxidizer and Fe^{2+} as catalyst and its technical process are studied in this paper. The study shows that Fe^{2+} can effectively catalyze the ammoxidation reaction, shorten the reaction times, decrease the reaction temperature and raise the efficiency of ammoxidation.

Key words:
Straw-pulp alkaline lignin, hydrogen peroxide, Fe^{2+} as catalyzer, ammoxidation

Introduction

Wheat straw, as well as other agricultural residues, are so abundant as to be an ideal alternative raw materials for papermaking, especially in China with dramatically growing demand for paper and minimal wood resources. The condensate of spent liquor from straw digestion is difficult to combust to recover the alkali because it has high silica content and high viscosity. This resulting black liquor from straw-pulp mills has become one of the most significant pollutants in China. Approaches have been sought to utilize straw-pulp lignin for many years to alleviate environmental load in China.

Lignin is one of the most abundant naturally occurring biopolymers. For many years its characterization has received great attention from agriculturists as a precursor to humic substances in soils.[1] Biological degradation of lignin is very slow due to its complex three-dimensional network structure and its high $\zeta_{C/N}$ ratio ($\zeta_{C/N}$ = 250).[1] It can act as inert carrier of slow-released fertilizer because it can be slowly degraded by microorganisms to release nutrients. Nowadays, the fertilizing effect of N-modified lignin is well recognized, which has been described elsewheres.[1–3]

Ammoxidation is an important way to turn straw-pulp lignin into a slow-release fertilizer. Conventional ammoxidation of lignin was conducted with oxygen at high pressure and at high temperature. The first attempt of ammoxidation to straw-pulp alkaline lignin using hydrogen peroxide as oxidizer at normal pressure and lower temperature was made by *Zhang Xiaoyong* in 1999.[9] In 1993, *Zúñiga*[6] pointed out that compounds of transitional metals such as iron(II), molybdenum, copper(II) and manganese catalyze to ammoxidation to some extent. In this paper, ammoxidation of straw-pulp alkaline lignin using hydrogen peroxide as oxidizer and iron(II) cation as catalyst has been reported.

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Materials and methods

Materials

In this experimental work, feedstocks are obtained from black liquor supplied by the Wugang paper mill in HeNan Province, P.R.China where wheat straw is cooked with soda as the only chemical. The straw black liquor, as produced, has a solid content ranging between 5 % and 10 % in mass. The black liquor was processed by dry fractionation to form feedstocks in this trial. The main process steps are acid precipitation, washing, drying, grinding and screening. The main components of feedstocks are: lignin 49.44 %; water 4.85 %, ash 12.85 %, C 51.38 %, H 5.54 %, and N 1.69 %.

Ammoxidation of wheat straw alkaline lignin by hydrogen peroxide

Ammoxidizing experiments were carried out using a 2 L batch cylindrical autoclave digester that was heated by means of electrical resistance and linked through a stirred axle to a control unit, including a motor actuating the reactor and the required instruments for measurement and control of pressure and temperature.

Powdered alkaline lignin, a preset amount of hydrogen peroxide (30 %) and ammonia liquor (25~28 %) were fed into the reactor. The temperature was increased from room temperature to the

preset maximum temperature and then kept constant for a given period of time. After reaction, the product of ammoxidation was spray-dried and nitrogen content was determined.

Analytical methods

Nitrogen content was estimated by micro-Kjeldahl method as the ammonia nitrogen content before sample is digested (expressed as A) and total nitrogen after digestion of the sample. Ammonia nitrogen subtracted from total nitrogen is 1-A which is an important index to evaluate ammoxidation. Organic nitrogen is an important index to ammoxidation due to its covalent bond between carbon and nitrogen, but uniform standard was not established in determination of organic nitrogen. Consequently, residual nitrogen except ammonia nitrogen expressed as 1-A should be the most important guide to ammoxidation in this experiment because its composition is mainly organic-compound nitrogen.

Results and discussions

Transition metal ions

Zúñiga (1993)[6] reported that compound of transition metals such as iron(II), molybdenum, copper(II) and manganese catalyze ammoxidation to some extent. In this experiment, the effect of four metal ions on ammoxidation is reported. Fe^{2+}, Mo^{6+}, Mn^{2+} and Cu^{2+} were injected into digester respectively. The product is determined after spray-drying.

Fig. 1 shows that transition metal ions play a minor role in ammoxidation. Compared to controls, 10 mg L^{-1} Mn^{2+} or Cu^{2+} do not have positive but inhibiting effect on nitrogen content of lignin. 10 mg L^{-1} Fe^{2+} and Mo^{6+} have slightly catalytic effects on the ammoxidation reaction, increasing nitrogen levels to 0.18 % and 0.24 % respectively. Unlike oxygen as oxidizer, transition metal ions have little effect on ammoxidation using hydrogen peroxide as oxidizer.

Concentration of Fe^{2+}

Ammoxidation of alkaline lignin is better assisted by catalyst when hydrogen peroxide is the oxidizer. Hydrogen peroxide can be easily degraded to decrease efficiency of ammoxidation in the reacting liquor. Fe^{2+} and Mo^{6+} have been reported[1] to have a catalytic effect on nitrogen fixation. As mentioned in Section 3.1, iron(II) cation is chosen as the best catalyst due to its abundancy and low price.

30g acid-precipitation lignin (2.1), 60 ml hydrogen peroxide (30 %) and 60 ml ammonia liquor were fed into autoclaved digester and distilled water was added to a total volume of 300 ml. The conditions to ammoxidize straw-pulp alkaline lignin are: reaction time 90 min, reaction temperature 120 °C and stirring speed n = 600 min^{-1}. Ammoxidation is conducted with Fe^{2+} at various concentrations (to mass fraction). Nitrogen content is determined after the ammoxidized products are spray-dried.

As can be seen in Fig. 2 low mass concentration (≤ 15 mg L^{-1}) of iron(II) cation have a slight catalytic effect on increasing the lignin nitrogen fraction. Since ammonia nitrogen decreases with the increasing Fe^{2+} concentration, the effect at concentrations lower than 15 mg L^{-1} Fe^{2+} is not remarkable. 1-A rises up slightly at low concentrations of Fe^{2+} but falls sharply at more than

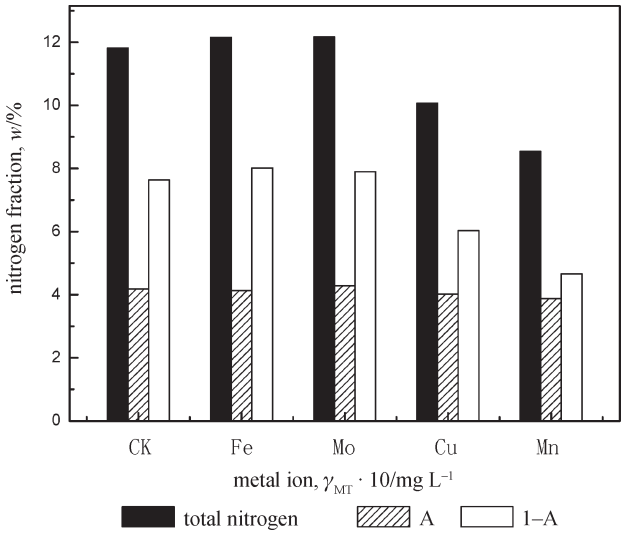


Fig. 1 – *Effect of transitional metal ion on ammoxidation under reaction temperature 120 °C, reaction time 90 min, ammonia charge 20 % and hydrogen peroxide charge 20 %*

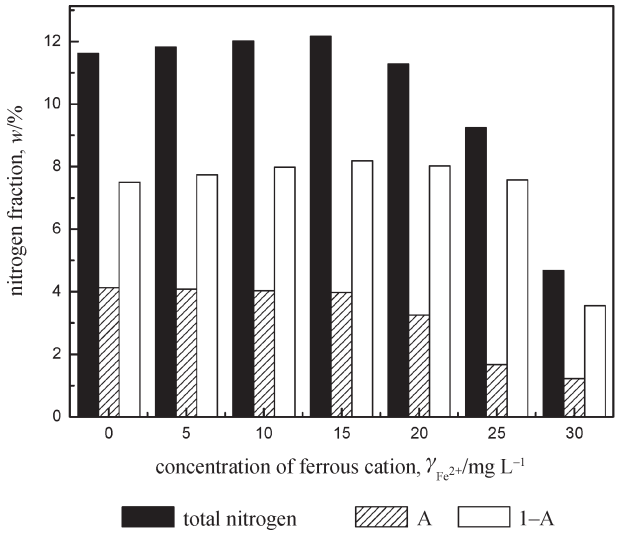
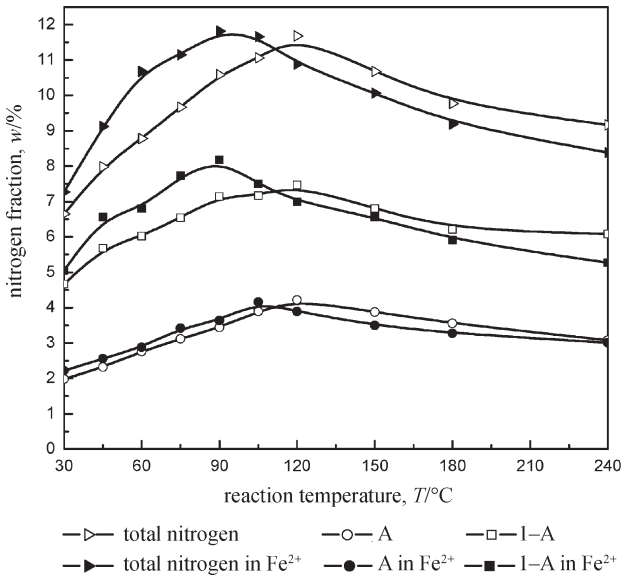


Fig 2 – *Effect of concentration of Fe^{2+} on nitrogen content of lignin under reaction temperature 120 °C, reaction time 90 min, ammonia charge 20 % and hydrogen peroxide charge 20 %*

25 mg L^{-1} Fe^{2+}. Total nitrogen is the highest with 15 mg L^{-1} Fe^{2+}, only 0.25 % nitrogen content is increased. 15 mg L^{-1} of Fe^{2+} is a suitable dosage for ammoxidation. However, iron(II) cation can give rise to other distinct changes to ammoxidation. The main changes of Fe^{2+} promoting ammoxidation are revealed by changes of technical quantities.

Reaction temperature

Operating conditions were maintained as described in Section 3.2, with other variables kept constant, the reaction temperature was set at increasing value from 30 to 240 °C, and the results were compared without any catalyst or with the iron(II) cation catalyst at the optimal mass concentration of 15 mg L^{-1}. Nitrogen fraction was determined on spray-dried ammoxidized products.



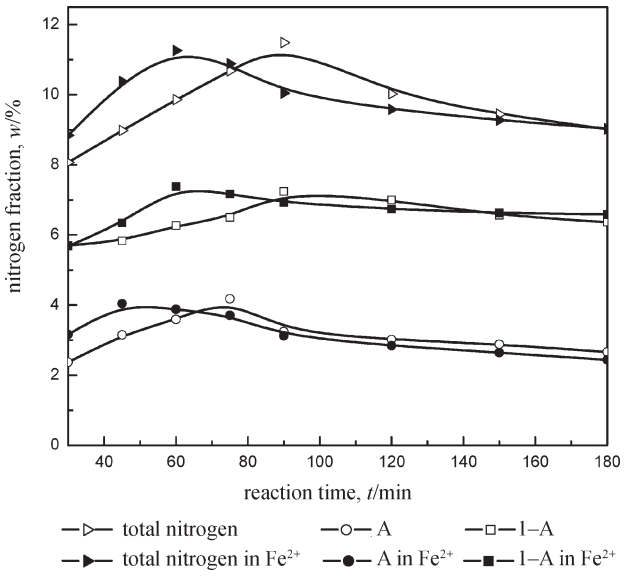
F i g 3 – *Effect of reaction temperature on nitrogen content of lignin with Fe^{2+}catalysis under reaction time 90 min, ammonia charge 20 % and hydrogen peroxide charge 20%*

A rise in temperature makes it possible to make the ammoxidizing reaction more quickly, but it also speeds up degradation of hydrogen peroxide, thus slowing down ammoxidation. From Fig. 3 we can see that total nitrogen, ammonia nitrogen and 1-A are maximized at 120 °C in the absence of Fe^{2+}. In the presence of Fe^{2+}, the highest point of ammonia nitrogen appears at 105 °C; at 90 °C, the highest organic nitrogen (1-A) level is 8.18 %, and total nitrogen is about 11.82 % at 90 °C; This last value is superior by 1.8 % with respect to the same without any catalyst at 120 °C. These results show that Fe^{2+} decreases the temperature of the system (by about 30 °C) and effectively increases the organic nitrogen content 1-A.

Reaction time

Reaction time dependence of ammoxidation is studied using the same experimental conditions as those described in 3.3. The reaction products, released by reaction pressure, are sampled every 15 min. Nitrogen content is determined after the ammoxidized products are spray-dried.

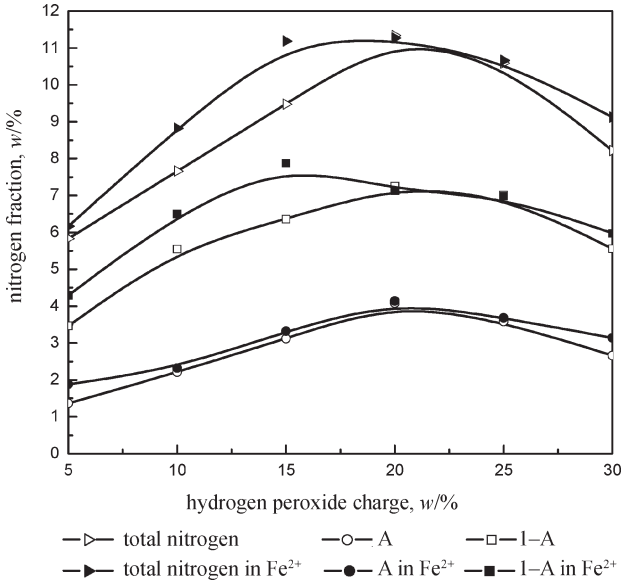
Reaction time is one of the most important quantity in the ammoxidation process. As shown in Fig. 4, the optimal reaction time of total nitrogen and 1-A is 90 min in the absence of iron(II) cation and 60 min with iron(II) cation catalysis, while ammonia nitrogen is maximized in 45 min as opposed to 75 min. In accordance with our expectation, catalysis by iron(II) cation makes it possible to shorten the reaction time for ammoxidation in a specific reaction time. Although total nitrogen is not raised, organic nitrogen (1-A) increases strikingly.



F i g . 4 – *Effect of reaction time on nitrogen content of lignin with Fe^{2+}catalysis under reaction temperature 120 °C, ammonia charge 20 % and hydrogen peroxide charge 20 %*

Hydrogen peroxide charge

Hydrogen peroxide charge is estimated with other independent variables kept constant. At 90 °C, 60 min and other quantities constant, the dosage of hydrogen peroxide is varied from 5 % to 40 %. Fig. 5 shows that the variation of ammonia nitrogen with Fe^{2+} catalysis is similar to that obtained with no iron(II) cation. A high yield of total nitrogen appears with both 15 % and 20 % hydrogen peroxide charges. With respect to 1-A, a 15 % load is suitable for Fe^{2+} catalyzed ammoxidation, when a 20 % load is optimal for uncatalyzed reaction.

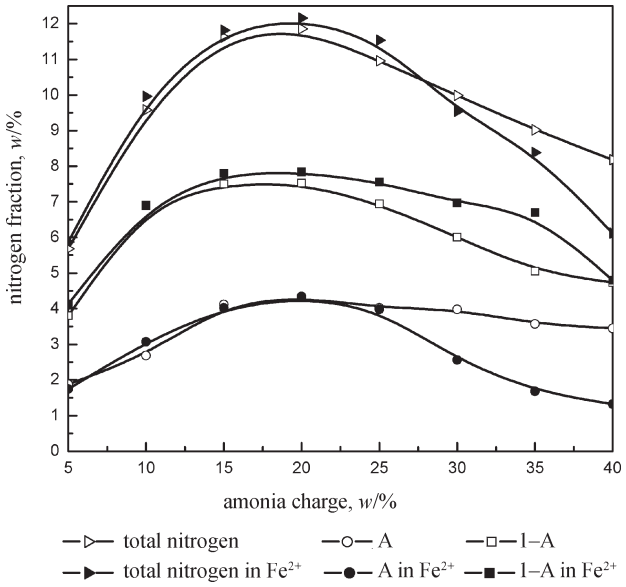


F i g . 5 – *Effect of hydroperoxide charge on nitrogen content of lignin with Fe^{2+}catalysis under reaction temperature 120 °C, reaction time 90 min and ammonia charge 20 %*

Ammonia charge

To study the effect of ammonia charge, the same experimental conditions are required as those described in section 3.4.

The results of Fig 6 are obtained using a similar procedure with other independent variables. Total nitrogen of the product from iron(II) catalyzed ammoxidation seems more sensitive to ammonia charge than the product from uncatalyzed reaction. However, above ammonia load threshold, the beneficial effect of iron(II) catalysis on total nitrogen increase is limited by pH increase. Organic nitrogen(1-A) is insensitive to variations in ammonia levels. The most prominent effect of the iron(II) cation on ammoxidation is the increased organic nitrogen(1-A).



F i g . 6 – *Effect of ammonia charge on nitrogen content of lignin with Fe^{2+}catalysis under reaction temperature 120 °C, reaction time 90 min and hydrogen peroxide charge 20 %*

Optimum techniques of ammoxidation by hydrogen peroxide as oxidizer and a brief analysis of catalysis of Fe^{2+}

From above discussion we can see that the desirable experimental conditions for the uncatalyzed ammoxidation are: reaction time 90 min, reaction temperature 120 °C, hydrogen peroxide charge 20 % and ammonia charge 20 %. Optimal ones for the Fe^{2+} catalyzed ammoxidation are: reaction time 60 min, reaction temperature 90 °C , hydrogen peroxide charge 15 % and ammonia charge 20 %.

Although Fe^{2+} cannot increase nitrogen content of lignin greatly, it improves the efficiency of ammoxidation and increases organic nitrogen(1-A). The reaction time is shortened by 30 min from 90 min to 60 min, reaction temperatures drop by 30 °C from 120 °C to 90 °C. This could be because the unstable hydrogen peroxide stabilizes by iron(II) cation. Some variation of pressure due to hydrogen peroxide feeding can be seen in the course of reaction. Ammoxidation is conducted in the stirred autoclave, a certain pressure is produced during reaction due to hydrogen peroxide feeding. The pressure fluctuates from 4 kg cm^{-2} to 8 kg cm^{-2} in the Fe^{2+}-free experiments, whereas with Fe^{2+}-catalysis, the pressure strolls in the scope of 5~6 kg cm^{-2}.

The reaction between Fe^{2+} and H_2O_2 can be conducted in the condition of alkalescence;

$$Fe^{2+} + H_2O_2 \xrightarrow{pH=9-11} Fe^{3+} + HOg + OH^-$$

When pH > 9.2, Fe^{2+} can generate hydrogen peroxide into $OH(g)^-$ free radicals that are highly reactive to lignin and increase nitrogen content of ammoxidized lignin by enabling the reaction ammonia with the newly formed oxygen functional groups. Ammoxidation is influenced by pH value when pH > 10. In addition, complexation between Fe^{2+} or Fe^{3+} and hydrogen peroxide can prevent invalid degradation of hydrogen peroxide. Therefore, it has the effect of promoting ammoxidation.

Ferrous cation makes it possible to ammoxidize alkaline straw-pulp lignin under normal pressure and lower temperature. It is vital to small-and medium-size paper mill which are widely scattered around in China. A promising approach will be offered to turn waste of straw-pulp mill into slow-release fertilizer.

Conclusion

(1) Iron(II) cation catalyzes ammoxidation of alkaline lignin with hydrogen peroxide as oxidizer, but this effect is not major; the increase in total nitrogen was only 0.25 %.

(2) Compared controls without Fe^{2+}, the technical parameters of ammoxidation with Fe^{2+} are greatly changed. The reaction is reduced by 30 min to 60 min, the reaction temperature is decreased by 30 °C to 90 °C. In addition, ammoxidation is more sensitive to variation of pH in the Fe^{2+} catalyzed case than in the no Fe^{2+} case and oxidation by hydrogen peroxide is more stable in the presence of Fe^{2+}.

List of symbols

n – stirring speed, min^{-1}
T – temperature, °C
t – time, min
w – mass fraction, %
γ – mass concentration, mg L^{-1}
ζ – mass ratio

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